COLLOIDAL NATURE AND RELATED PROPERTIES OF CLAYS

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ABSTRACT

A theory is presented on the colloidal nature and related properties of clays, based upon the findings of certain soil scientists and the existing knowledge of the phenomena of coagulation, deflocculation, plasticity, drying shrinkage, and dry transverse strength. It is thought that this paper will allay some of the present confusion of ideas concerning the subject of clay colloids by adaptation of this theory to furnish a more satisfactory explanation of the above phenomena.

CONTENTS

I. INTRODUCTION

A review of the ceramic literature yields a confusion of ideas concerning clay colloids. Ceramists have thus far advanced no complete theory capable of explaining clearly the mechanism of the phenomena of deflocculation, coagulation, plasticity, drying shrinkage and dry strength of clays and the variation of these properties caused by variations in the treatment of a given clay. The general impression gained from the early literature is that clays are composed of extremely small, negatively charged, active colloid particles covering the surfaces of larger inert particles. This thin coating of colloidal particles is said to account, in varying degrees, for the above phenomena, but the explanation of the chemistry or physics involved seems always to be hazy. For example, at what size does a particle cease to be an active colloid and become inert and why has the larger particle no charge if the smaller one of like composition has a negative

charge? The variation in ideas concerning this general subject can be found in comparatively recent papers.[1][2][3][4][5][6]   Vickers mentioned the subject of base exchange; Hissink gave the manner in which exchangeable bases occur on the clay particle.   Marshall went into the subject in more detail and also pointed out the fact that colloidality of clays increases with a decrease in particle size, thus apparently not considering the colloids as a separate and distinct group of particles, as most writers had done previously.

Theories capable of explaining quite satisfactorily the behavior of soil colloids have been advanced by Mattson.[7]   Certain of these theories, if properly interpreted, can be used to explain the phenomena exhibited by ceramic clays and clay colloids.   After digesting the voluminous and detailed works of Mattson and the writings of others, the author of this paper presents, with some modifications or added interpretations where these are justified or necessary, such of the theories as are needed to account for the behavior of ceramic clays and clay colloids.   The adaptation of the theories to the known facts is attempted in the latter part of this paper.

In order to simplify the explanations of various reactions it will be necessary to assume, in some cases, ideal conditions which may never quite exist, as for example, equilibrium between the clay and the weathering solution or the suspending medium.

II. TERMS AND DEFINITIONS

It is thought that the following terms and definitions, most of which are well known in the field of soil science, might be of assistance to those readers who are unfamiliar with this field.   The symbols in brackets at the end of each definition correspond with the symbols in figure 1.

Clay particle.—A core composed of one or more molecules, and carrying on its surface basic and acidic groups or atoms, or positive and negative ionic charges, or both.   [(1) plus (2)].

Micellar ion atmosphere.—An atmosphere of adsorbed and unadsorbed ions surrounding the particle.   [(3)].

Micelle.—The clay particle, its ionic atmosphere and imbibed water (see section VI).   [(1) plus (2) plus (3)].

Intermicellar ions.—Ions in solution outside of the micellar atmosphere [(−) and (+) in zone (4)].

Colloid complex.—The active particle surface together with its micellar ion atmosphere and imbibed water [(2) plus (3)].

Acidic constituents.—Those integral components of the particle which have a negative ionic charge when ionized (the acid radicals of weak acids) [A].

Amphoteric constituents.—Those integral components of the particle which ordinarily have a positive ionic charge when ionized, but can have a negative charge [B].

Ionic charges (on the particle surface).—Positive and negative charges at the particle surface resulting from ionization of acidic and basic residues or their reaction products [+ and − in zone (2)].

[1] McDowell, J. Am. Ceram. Soc., [4]10, 225(1927).
[2] Vickers, Ceram. Soc. Trans., 28,91 and 124(1929).
[3] Hall, Jour. Am. Ceram. Soc.. [10]13,751(1930).
[4] Marshall, Ceram. Soc. Trans., 30,81(1931).
[5] Hissink, Trans. Faraday Soc., 20,551(1924–25).
[6] Ashley, Techn. Pap. BS.23, 33(1911).
[7] Soil Science, 30,459(1930); 31,311(1931); 32,343(1931); 33,301(1932); 34,209 and 459(1932).

Adsorbed atoms or groups.—Basic and acidic atoms or groups held on the surface of the clay particle by valence bonds $\bigcirc$ in zone (2)].

Adsorbed ions.—Those ions held in the atmosphere about the clay particle by opposite ionic charges on the particle surface [$\oplus$ and $\ominus$ in zone (3)].

Unadsorbed micellar ions.—Ions in the micellar atmosphere not held by opposite ionic charges on the particle surface (see section VI). [(+) and (−) in zone (3)].

Acidic residue.—That portion of the acid remaining unneutralized after reaction (partial combination) of a weak acid with a weak base, e.g., compare partial neutralization:

$3H_2SiO_3 + 2Al(OH)_3 \rightarrow H_3(3SiO_3 \equiv 2Al)(OH)_3 + 3H_2O$, with complete neutralization:

$$3H_2SiO_3 + 2Al(OH)_3 \rightarrow (3SiO_3 \equiv 2Al) + 6H_2O.$$
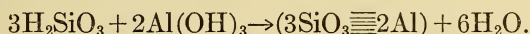
Basic residue.—That portion of the base remaining unneutralized after reaction (partial combination) of a weak acid with a weak base.

Acidoid.—A colloid which reacts as an acid, e.g., colloidal silicic acid.

Ampholytoid.—A colloid which can act either as an acid or as a base depending upon its environment, e.g., colloidal aluminum and ferric hydroxides. (It is said that there are no basoids.)

Silica:Sesquioxide ratio.—A term commonly used to express the ratio of acidic to amphoteric constituents or the acidoid to ampholytoid ratio of soil and clay colloids, because silicic acid and aluminum and ferric hydroxides are the chief reactants in the formation of these colloids. [Numerically this ratio is equal to $2A/B$].

III. THE CLAY PARTICLE AND THE COLLOIDAL COMPLEX

1. FORMATION OF CLAY PARTICLES

From Mattson's work [8] it is apparent that completely weathered clays are made up of particles of various sizes, formed by the reaction (partial or complete combination) of weak acids, e.g., silicic acid, and weak bases, e.g., aluminum and ferric hydroxides, derived from the parent rock. The particles formed will be crystalline or amorphous, depending upon existing conditions. In either case there will be acidic and basic residues at the particle surfaces (fig. 1).

It can be seen from the illustration that this surface condition exists regardless of the particle size and therefore any property caused by it would be more likely a function of specific surface than of the percentage of material below a given particle size.

According to Mattson the acidic and basic residues of the particle are free to react, under favorable conditions, with other constituents of the clay or leaching solution. That is, the particle can grow through displacement of the hydroxyl group and the hydrogen by more of the acids and bases already present, or by other anions and cations in the weathering solution, which, upon uniting with the particle, will hinder or arrest further growth if they do not fit into its internal structure. For this reason the presence in the weathering solution of material foreign to the pure end product of the weathering process will retard the formation of the end product. The anions or

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[8] See footnote 7, p. 246.

cations reacting with the basic or acidic residues of the particle may be monovalent, e.g., Cl^- or Na^+, polyvalent, e.g., PO_4^{---} or Ca^{++}, or more complex ions such as $\left(-Al\diagup^{OH}_{OH}\right)^+$ or $(H-SiO_3-)^-$. A polyvalent ion may unite with the clay particle by one bond and then with one or more ions of opposite charge, depending upon the number of remaining valences (fig. 2). In this manner, a layer of varying degree of heterogeneity, depending upon the prevailing conditions, might be built up on the surface of the clay particle.

An ion of sufficient concentration might even replace some of the acidic or basic constituents of the particle. However, such ionic concentrations are probably not common in normal weathering or
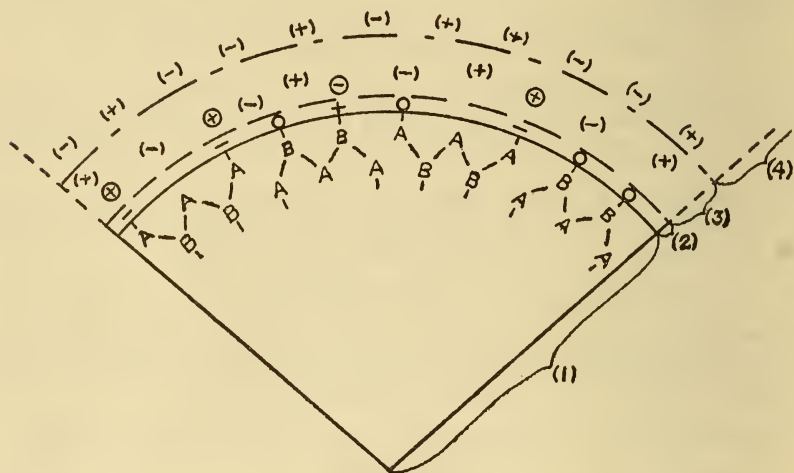

FIGURE 1.—*Portion of a hypothetical clay micelle, showing the component parts.*
[See text, p. 247.]

ceramic processes. It is believed that by far most of the reactions of the clay, which are dependent upon the acidic and basic residues, take place at the particle surfaces and hence are a function of the specific surface of the clay.

2. COLLOID COMPLEX—THE SOURCE OF COLLOIDALITY OF CLAYS

The outside layer of the clay particle together with its adsorbed ions is called the colloidal complex, since nearly all of the reactions which give clays colloidal properties take place here. The upper limit of colloidal particle size has been accepted by most workers in colloid chemistry as 0.1 micron in diameter. However, English china clays exhibit colloidal properties to some degree and yet Marshall[9] found that they contained practically no particles less than 0.1 micron in diameter. The soil chemists have accepted 2 microns as the diameter of the largest particles exhibiting colloidal properties.[10] The lack of a definite upper size limit of colloidal clay particles may be explained if it is assumed that the whole particle is not necessarily

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[9] See footnote 4, p. 246.
[10] U.S. Dept. of Agri., Tech. Bull. 170.

colloidally active, but that it has a stable core with an active surface. It can readily be seen that a clay composed of two-micron particles with a very active surface complex might exhibit colloidal properties to a greater extent than a clay composed of one-micron particles with a much less active surface complex. The exhibition of colloidal properties would, therefore, depend not only upon particle size but also upon the activity of the surface layer.

IV. RELATION OF pH OF WEATHERING SOLUTION TO COMPOSITION AND ISOELECTRIC pH

It was pointed out that, under favorable conditions, the clay particle could enter into various reactions. These conditions depend upon the concentrations of the various ions present. Even at the isoelectric point, in which condition a clay is most stable, the acidic and basic residues are ionized to some extent. By definition [11] the positive charges on the particles equal the negative charges at the isoelectric point (or $H^+ = OH^-$), regardless of the ratio of acidic to basic residue. This condition might be represented by figure 3.

It can be seen that particle (a) would be isoelectric at a lower pH value than would particle (b) because the former would require more hydrogen ions in solution to suppress the ionization of the hydrogen atoms on the particle. Thus, the higher the ratio of the acidic residue to the basic residue of the particle, the lower will be the isoelectric pH.[12]

Since clay is most stable at its isoelectric point, it will tend to weather to that composition which is in the isoelectric condition at the pH value of the weathering solution. This has been found to be the case in nature.[13] In cold, damp climates, where the pH values of the weathering solutions are low, the product has a higher ratio of acidic to amphoteric constituents (silica to sesquioxides) than in moist warm climates, where the pH values of the weathering solutions are higher. To explain this, suppose particle (a), figure 3, is isoelectric at pH 3. If it is leached by a solution having a pH value
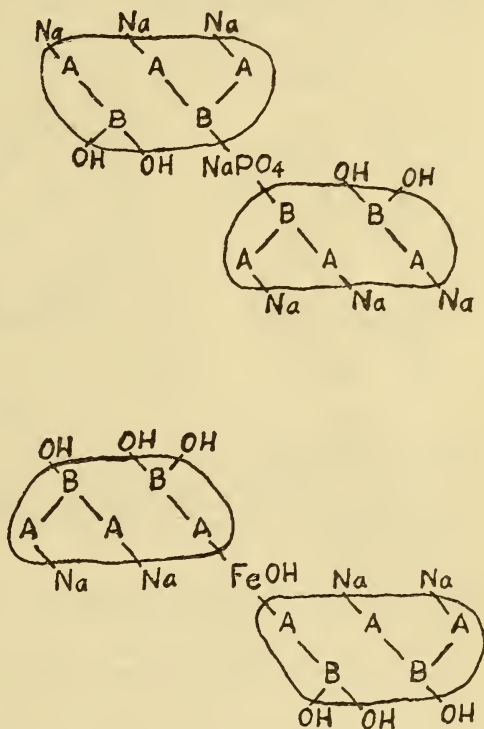

FIGURE 2.—*Mutual bonding of particles by polyvalent ions.*

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[11] Soil Sci., 34, 209 (1932).   [12] See footnote 11.   [13] See footnote 11.

of 5, the ionization of the hydroxyl groups will be suppressed and of the hydrogen atoms will be encouraged. Now, if the solution contains such ions as $\left(-Al{\displaystyle{OH \atop OH}}\right)^{+}$, they will displace hydrogen ions and combine with the particle. This change will decrease the ratio of acidic to amphoteric constituents (acidoid to ampholytoid ratio), thus lowering the ratio of acidic to basic residue, until the hydrogen and hydroxyl ions dissociated from the clay particle are again equal in number. Suppose particle (b), figure 3, is isoelectric at pH 5. If it is leached by a solution containing such ions as $(H-SiO_3-)^{-}$ and having a pH value of 3, the ionization of the residual hydrogen atoms will be suppressed and of the hydroxyl groups will be encouraged, resulting in the displacement of the latter by the above complex ion which will combine with the particle. This change will increase the ratio of acidic to am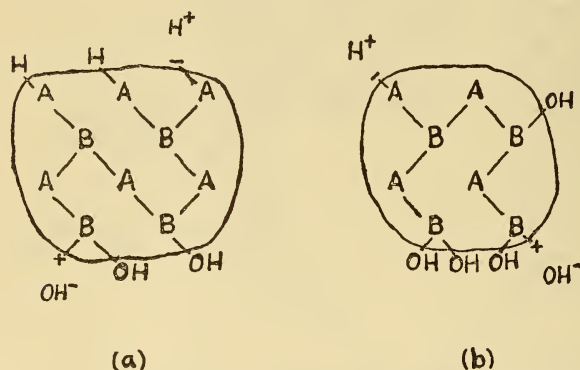photeric constituents, thus lowering the ratio of acidic to basic residue until the hydrogen and hydroxyl ions dissociated from the particle are again equal in number.

It is conceivable that colloidal clay particles can be composed of any number of molecules of any size, the atoms and molecules being held together by various types of valences. There may be almost any imaginable ratio of acidic to amphoteric constituents within these molecules or particles, depending upon their environment during formation. The ratios with which we are familiar persist because on combining in these ratios, weather-resistant minerals are formed.

FIGURE 3.—*Portions of clay particles in the isoelectric condition, showing the effect of the ratio of acidic (A) to amphoteric (B) constituents upon the ratio of acidic to basic residues at the surface; (a) beidellite ratio; (b) kaolinite ratio.*

Clay particles hold hydroxyl groups more strongly than they do hydrogen atoms. If this were not so, a clay of the composition of particle (a), figure 3 (which corresponds to that of the mineral beidellite), would have an isoelectric pH of 7, whereas actually its isoelectric point is at a much lower pH value.

V. ULTIMATE pH, EXCHANGE NEUTRALITY AND EXCHANGE CAPACITY

In figure 3 the clay particles were represented as completely unsaturated, i.e., free from any adsorbed ions, atoms or groups other than hydrogen and hydroxyl. This condition is obtainable by leaching the clay sample with distilled water to remove soluble salts and then electrodialyzing it. In electrodialysis a direct current is passed from an anode through the clay suspension, which is held by a porous membrane, to a cathode. Hydrogen ions, produced by the electric current, are carried through the clay in sufficient concentration to dis-

place the adsorbed bases, which are carried through the porous membrane to the cathode by the current and removed by constant flow of water. Furthermore, figure 3 shows the particles to be in the isoelectric condition. To arrive at this condition it is necessary to add to the suspension of electrodialyzed clay sufficient reagent to bring the water to the isoelectric pH of the clay. The pH value of the suspension of the electrodialyzed sample is called the ultimate pH, which lies between pH 7 and the isoelectric pH.[14] It varies with the concentration of the suspension, approaching the isoelectric pH as the concentration increases, and is conveniently determined in a suspension of one gram of material in 25 ml of distilled water.

The pH of exchange neutrality is that point at which the clay particles adsorb equal numbers of the cations and anions of a neutral salt,[15] and it differs for different salts. This condition is illustrated in figure 4.

The ultimate pH can be determined by adding one gram of the electrodialyzed, dried and pulverized clay to 25 ml of distilled water and determining the pH the following day. The pH of the original clay could be determined in the same manner. To determine the pH of exchange neutrality and the exchange capacity of a clay at any pH,[16] make up stock solutions of 0.1 normal sodium chloride, containing 0.0, 0.05, 0.1, 0.2, and 0.3 milliequivalent of added sodium hydroxide and 0.05, 0.1, and 0.2 milliequivalent of added hydrogen chloride, respectively, per 25 ml of solution. First determine the pH value of each of the solutions and plot them against the milliequivalents of added acid or base. This will give the curve for the neutral salt solution (fig. 5). Now leach and electrodialyze 10 grams of clay (preferably using the Salgado and Chapman cell).[17] Dry on a water bath and pulverize
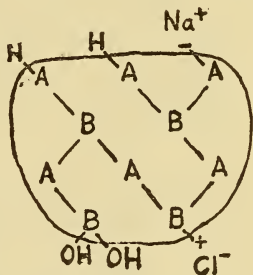

FIGURE 4.—*Portion of a clay particle in the condition of exchange neutrality.*

the electrodialyzed clay and add 1 gram to 25 ml of each of the stock solutions. Shake one-half hour, let stand over night and determine the pH of each. Plot the curve for pH versus milliequivalents of added acid or base. The point at which the curve for the clay suspension intersects that for the neutral salt solution represents the pH of exchange neutrality. At any given pH, the horizontal distance between the two curves represents the exchange capacity of the clay in equilibrium with the neutral salt (sodium chloride) for chlorine or for sodium, as the case may be.

The increase in base exchange capacity of a given clay with an increase in pH value must have an upper limit for the same reason that there is a lower limit in pH value at which maximum anionic adsorption occurs, i.e., a change occurs in the nature of the clay particles.

If the combination of the clay with the cations of the salt has the same stability as that with the anions of the salt, the pH of exchange neutrality will be the same as the isoelectric pH.[18] This is practically true for sodium chloride.[18] If sodium sulphate were used the sulphate, forming a more stable compound with the clay (being more strongly adsorbed), would displace more hydroxyl ions than the num-

[14] See footnote 11, p. 249.
[15] See footnote 11, p. 249.
[16] This procedure varies slightly from that of Mattson; Soil Science, 34,459(1932).
[17] Soil Science, 32,199(1931).
[18] See footnote 11, p. 249.

ber of hydrogen ions displaced by the sodium, thus giving the suspension, at exchange neutrality, a pH higher than the isoelectric pH.

The degree of dissociation of a salt formed by union of ions with a given clay particle depends upon the ions entering into this union. The decreasing order of this degree of dissociation for some cations and some anions seems to be $Na > K > Ca > H > Fe > Al$ and $Cl > SO_4 > SiO_3 > PO_4 > OH$.[19] The Hofmeister series, which takes into account both valence and the nature of the ion, seems to obtain.[20]   The
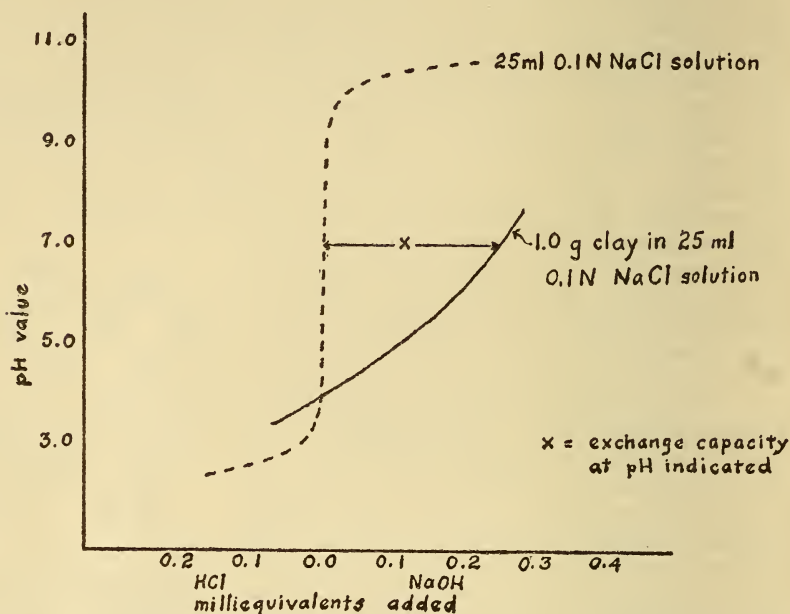

FIGURE 5.—*Determination of* pH *of exchange neutrality and exchange capacity (from Mattson with slight modification).*

order of the stability of the compounds formed by these ions with clay particles is the reverse of the above.

It has been shown [21] that, with a given sesquioxide composition, an increase in the silica to sesquioxide ratio of the particle causes a decrease in the pH of exchange neutrality (and for that matter, also of the isoelectric pH and the ultimate pH, since they are not greatly different). Mattson [22] has found that a substitution of iron for aluminum in the sesquioxide lowers the pH of exchange neutrality on account of the less nearly complete combination between iron and the silicate than between aluminum and the silicate, thus making available more acid residue and hence increased absorption capacity for cations (or base exchange capacity). Incidentally, the adsorption capacity for anions is increased a like amount by this less nearly complete combination, but the great stability of the hydroxyl-clay complex prevents appreciable displacement of the hydroxyl ions until a very low pH is reached. Displacement of silicate by humate or phosphate has an effect on exchange neutrality and exchange capacity similar to that of replacing aluminum with iron.[23] The effect of the

[19] Soil Science, 34,459(1932).
[20] Soil Sci., 33,301(1932).
[21] See footnote 19, p. 252.
[22] See footnote 19, p. 252.
[23] See footnote 19, p. 252.

latter replacement might be represented by a comparison of H_3 $(3SiO_3 \equiv 2Al)$ $(OH)_3$ with H_4 $(3SiO_3 = 2Fe)$ $(OH)_4$.

It should be borne in mind that the presence of clay minerals, which contain as integral parts of their structure alkali or alkali earth atoms, will, if Marshall [24] is correct in his statement that these atoms are exchangeable, modify the relation between the exchange capacity at a given pH and the acidoid to ampholytoid ratio of the particle surfaces. Internal base exchange will also affect the relation between base exchange capacity and those properties which depend upon the activity of the particle surfaces; for the occurrence of internal base exchange would result in a less active surface than that indicated by the relation between exchange capacity and specific surface.

VI. WATER OF OSMOTIC IMBIBITION [25]

Before discussing imbibed water it might be well to mention briefly the three other types of water common to clays. They are (1) combined water, held in the form of hydrous oxides; (2) hygroscopic water, held on the particle surfaces by molecular attraction; (3) capillary water, held in fine capillaries and interstices by surface tension. The hygroscopic water is very firmly held in a layer which has been variously measured as 2.5 to 5.0 millimicrons in thickness.[26] This layer is practically rigid because of the force with which it is held. It is evidenced by heat of wetting and by compression of the solid particles.

Up to this point exchange reactions have been represented as direct combinations of ions with clay particles by the conventional valence bonds. Now it is convenient and logical to make use of the double layer theory. The surface of the clay particle is covered, more or less thickly, depending upon its composition and the pH of its suspension, with a layer of positive and negative ionic charges. The algebraic sum of these charges is positive when the pH of the surrounding solution is below the pH of exchange neutrality (because of the high concentration of H^+ ions which neutralize the negative ionic charges), making possible adsorption or attraction of anions,[27] and negative when the pH of the solution is above this pH, making possible adsorption or attraction of cations. The latter condition is the one most common to ceramic clays and processes. Outside this layer is the second layer composed of an atmosphere of adsorbed diffusible ions, bringing the micelle, as the whole is called, into equilibrium with the surrounding or intermicellar solution, according to the Donnan equilibrium equation.[28]

$$x^2 = y(y + z)$$

where:

    x = ionic concentration of the cations and of the anions in the intermicellar solution (total = $2x$).

    y = ionic concentration of the cations and of the anions in the micellar solution (total = $2y$).

    z = ionic concentration of the adsorbed ions, i.e., the ions whose charges are attracted by the clay particle.

[24] See footnote 4, p. 246.
[25] See footnote 20, p. 252.
[26] See footnote 20, p. 252.
[27] As shown in Mattson's work, see footnote 19, p. 252.
[28] See footnote 20, p. 252.

This condition of equilibrium might be represented by figure 6. The osmotically imbibed water is held by this ion atmosphere surrounding the clay particle in a layer of varying thickness and viscosity depending upon the density and thickness of the atmosphere. It is self-evident that:

$$(2y+z) - 2x = e = \text{excess micellar ions}$$

Therefore, since the osmotic pressure in the micelle is proportional to the excess (e) [29] of ions present, it can be seen that a decrease of "z" caused by substitution of an ion lower in the Hofmeister series (calcium) for one higher in the series (sodium) or an increase in "x" (with "z" constant) caused by addition of free electrolyte to the intermicellar solution, would reduce the amount of imbibed water per unit surface of the particle. This relation has been proved by experiment.[30]

The base exchange capacity of a clay, at any given pH, indicates its capacity for osmotic imbibition of water when saturated with a given ion at that pH. The imbibition is evidenced by swelling of the
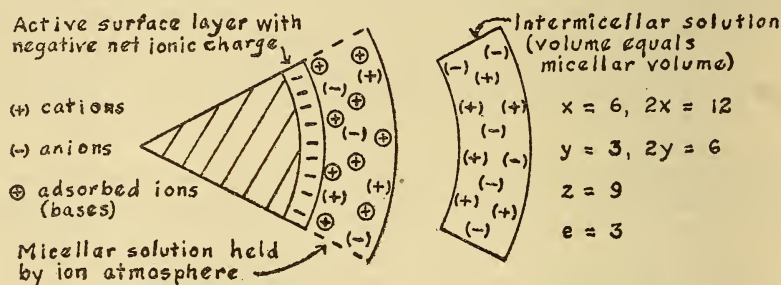

FIGURE 6.—*Donnan equilibrium condition (from Mattson with slight modification).*

clay mass. Tests on fine fractions of various soils and clays have shown that a very active particle surface may cause imbibition of a layer of water up to 23 to 45 millimicrons in thickness when treated with an ion such as sodium. This thickness was calculated by the author from Mattson's data on average particle size and imbibitional swelling.[31] To illustrate the effect of particle size let us assume three spherical particles, 10 microns, 1 micron and 0.1 micron in diameter, respectively, each imbibing a layer of water 25 millimicrons in thickness. The volume of water imbibed by the 10-micron particle will be 1.5 percent, by the 1-micron particle 15.8 percent, and by the 0.1-micron particle 238 percent of the original volume of the particle. It is evident that, other conditions being constant, the colloidality of a clay (if we assume imbibition to be a distinctly colloidal property) increases greatly as the particle size decreases or the specific surface increases.

Mattson found [32] that the imbibed water in a clay can be removed by application of pressure, the volume removed being proportional to the cube root of the pressure applied. He states that this relation is caused by the increase in osmotic pressure as the micellar ion concentration increases on approaching the particle surface.

[29] See footnote 20, p. 252.
[30] See footnote 20, p. 252.
[31] See footnote 20, p. 252.
[32] See footnote 20, p. 252.

VII. APPLICATION TO CERTAIN CERAMIC PHENOMENA

1. COAGULATION AND DEFLOCCULATION

In practically all literature on the subject [33] [34] deflocculation of clay suspensions has been attributed to the repulsion of particles of like charge, while coagulation is said to be due to the neutralization of the charges on the particles. The negative charges on the clay particles are assumed to be the result of selective adsorption of the hydroxyl ion.

According to the theory presented here it is true that the particle proper has a negative net ionic charge increasing from just above the isoelectric pH, at which the net charge of the particle proper is zero, to a maximum at the pH of maximum deflocculation. This negative ionic charge is due to the increased dissociation of adsorbed basic atoms or groups and the decreased dissociation of adsorbed acidic atoms or groups from the clay particle as the pH of the suspending medium is increased. Now, if at the same time the pH is increased a cation high in the Hofmeister series is added to the suspension in sufficient concentration to replace the adsorbed ions lower in the series, the number of ionic charges on the clay particle proper will be further increased. However, for every negative ionic charge on the particle there is a positive ionic charge on a cation in the micellar atmosphere and even though they may not neutralize each other completely individually, the net negative charge of the particle will always be equal to the net positive charge of its atmosphere under equilibrium conditions. It is reasonable to believe that two such micelles approaching each other in suspension would be repelled by the like net ionic charges of their particles and of their atmospheres but would be attracted an equal amount by the unlike net ionic charges of the particle of each and the atmosphere of the other.

The motion of the particle in an electric field is caused by upsetting the equilibrium or changing the potential between the particle surface and its ion atmosphere, the cations being attracted by the cathode and the negative particle by the anode. At the isoelectric pH there is zero potential between the particle and its atmosphere and hence an electric field produces no motion of the particle.

In the coagulated condition the layer of imbibed water is thin and hence the clay particles are close enough together to attract each other molecularly. Also, the presence of polyvalent ions would make it possible for one ion to neutralize opposite ionic charges on more than one particle, thus holding the particles together. This phenomenon has been investigated by Marshall,[35] who advances the theory of orientated coagulation of clay particles by polyvalent ions.

In the deflocculated condition the clay particles are surrounded by imbibed water layers of sufficient thickness to prevent their molecular interattraction to any extent. This theory explains the greater ease of deflocculating such clays as ball clays, which imbibe large amounts of water, as compared to china clays and kaolins, which have less active particle surfaces. This theory will also explain many of the differences in actions of the various deflocculating agents. The monovalent deflocculating ion minimizes coagulation because it

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[33] See footnote 1, p. 246.
[34] See footnote 3, p. 246.
[35] See footnote 4, p. 246.

cannot ordinarily act as a bond between particles.   Sodium hydroxide increases the pH of a clay suspension more than does sodium silicate, if equal amounts of sodium are added in both cases.   The reports made by McDowell [36] concerning pH values of clay slips in the condition of maximum deflocculation are supporting evidence.   The more potent deflocculating action of sodium silicate as compared to sodium hydroxide may be explained by the fact that the silicate ions have the effect of increasing the acidoid to ampholytoid ratio of the surface layer of the particle, thus creating more surface activity.

2. PLASTICITY

The plasticity of a clay depends upon the number, thickness, and viscosity of the liquid films surrounding the particles in a given mass and also upon the shape, size distribution, and degree of aggregation of the particles.

The number of films is governed by the number of particles in, or the surface factor of, a given mass of clay, and is in turn a factor in determining the amount of deformation possible without rupture. The thickness of the liquid films regulates the distance between particles, hence the force of molecular attraction between them, and thus influences the force necessary to cause deformation of the mass.   The viscosity of the imbibed water films also influences the force necessary to deformation, and is inversely proportional to some function of the film's thickness or the excess micellar ion concentration. Shape, size distribution, and degree of aggregation of the particles will affect the ease with which they will slide or roll over one another (ease of deformation) and also the amount of interstitial space filled by capillary water.   The amount of this capillary water will be governed also to some extent by the thickness of the imbibed water films and will in turn influence the consistency of the mass.   Possibly the adhesion tension between the clay and the water as discussed by Clark [37] has some influence on plasticity (and deflocculation), but, in view of the work of Mattson previously cited, the conclusion that addition of small quantities of alkalies decreases the thickness of the "absorbed" (imbibed) water films, causing deflocculation, would seem erroneous.

Consider the plasticities of a comparatively coarse-grained kaolin and a fine-grained ball clay.   The former will contain fewer and probably thinner imbibed water films, and will imbibe a smaller percentage of the total water necessary to produce plasticity.   Due to the greater force between adjacent particles the kaolin will tend to form aggregations which will cause it to retain larger amounts of capillary water and also give the effect of increased particle size. The larger percentage of the more loosely held and less viscous capillary water will result in a softer mass, while the fewer and thinner water films will allow less deformation before rupture takes place.

3. DRYING SHRINKAGE

Drying shrinkage is caused by removal of capillary, imbibed, and usually some hygroscopic water.   The first and last depend chiefly upon particle size (or specific surface) and aggregation.   The amount

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[36] See footnote 1, p. 246.
[37] Trans. Cer. Soc. (Br.), **32**, 1(1933).

of water imbibed by the clay depends upon surface area and activity and the concentration and identity of the ions present.

Some of the differences between ball clays and china clays, with respect to the effect of forming pressure on shrinkage during drying and during heat treatment [38] might be explained by variations in the number of adsorbed ions and hence in the imbibed water. The amount of exchangeable bases present will in most cases be some function of the product of the number and thickness of water films separating the particles in a given mass.

4. DRY TRANSVERSE STRENGTH

Dry transverse strength is undoubtedly related to base exchange capacity. This is indicated by the low strengths of china clays and kaolins, which have low exchange capacities,[39] medium strengths of ball kaolins and some (usually light colored) ball clays, which have medium exchange capacities, and high strengths of dark ball clays and some of the common clays [40] high in iron and other impurities, which have high exchange capacities. There are other factors which affect dry transverse strength, but their importance does not outweigh that of the base exchange capacity. Clays have been strengthened by the addition of organic matter which undoubtedly increased the base exchange capacity.

The micellar ions and also any solute which might be left by evaporation of the suspending solution undoubtedly act as a cementing bond between the particles of the dried clay mass. The valence of the adsorbed ion might be an important factor, but this phase of the subject has not yet been investigated.

The fact that some clays have a higher dry transverse strength after addition of some nonplastic material can be attributed to one or both of two reasons: (1) Reduction of the shrinkage, eliminating microscopic drying cracks caused by strain from excessive shrinkage of the clay alone; (2) production of a particle size distribution which results in a smaller percentage area of voids in the cross section of the test specimen.

VIII. DISCUSSION AND SUMMARY

Clay particles are formed by the partial or complete combination of weak acids and weak bases, the ratio of the combination depending upon the pH value of the weathering solution. Basic and acidic residues occur at the particle surfaces, and can dissociate to form an ion (or micellar) atmosphere, leaving ionic charges on the particles. The degree of ionization of these adsorbed atoms and groups is controlled by the concentration of like ions in the intermicellar solution. The ratio of acidic to basic residue of the particle depends upon the composition of the surface layer (which, due to changing conditions, might be different from that of the interior). The nature and number of the micellar ions influence various properties of the clay.

The clay tends to weather to the composition which has an isoelectric pH value equal to the pH value of the weathering solution. For

[38] A. E. R. Westman; J. Am. Cer. Soc., [6]16, 256(1933).
[39] T. A. Klinefelter, W. W. Meyer, and E. J. Vachuska; J. Am. Cer. Soc., [6]16, 269(1933).
[40] T. A. Klinefelter, National Bureau of Standards, Properties of Some Ohio Red-burning Clays (Unpublished).

this reason the more completely a clay is weathered by a given solution, the less fine particles it will contain because it reaches the isoelectric composition. In this condition there is a minimum density of the micellar ion atmosphere, and maximum particle growth resulting from combination of the acidic and basic residues of adjacent particles. A low ratio of acidic to amphoteric constituents (silica to sesquioxide ratio) also corresponds with a low micellar ion density; hence it might be said that the amount of fine particles or the specific surface of a clay, and therefore the "colloidal content", varies inversely with the pH value of the weathering solution and the completeness of weathering. Since weathering is retarded by the presence of impurities we might expect the clay particles in impure clays to be finer grained than those in pure clays.

The colloidal properties of a clay are due to the presence of the ionic atmosphere mentioned above. The maximum size of particles which can exhibit colloidal properties depends upon the activity of their surface layers, which in turn depends upon their compositions. An increase in the ratio of acidic to amphoteric constituents (silica to sesquioxide ratio), or substitution of iron for aluminum or humic acid for silicic acid increases the activity. Osmotic imbibition of water, which depends upon the micellar ion atmosphere, accounts in large measure for the colloidal properties of clays. The base exchange capacity, at a specified pH value, is indicative of a clay's capacity for imbibed water, under given conditions.

Mattson [41] has suggested that soils might be classified chemically as to strength and capacity to react; the strength being indicated by the pH of exchange neutrality and capacity to react by the base exchange capacity at some given pH value. The same could be done for ceramic clays. The determination of these properties, as outlined in this paper, would not only furnish a means of classification, but would yield information which could be applied to the problem of clay beneficiation. There is need of experimental work in applying the theories presented in this paper to the solution of problems involving deflocculation, coagulation, plasticity, drying shrinkage and dry strength of various clays and bodies.

WASHINGTON, June 26, 1934.

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[41] See footnote 19, p. 252.